Experiment 5: Chemical Reactivity of $\text{Me}_2\text{SiCl}_2$: Formation of Silicone Oils, Silicone Polymers, and Borosilicate Ceramics

Introduction
Silicon is one of the most abundant elements on this planet. It is a major component of most minerals (silicates) that form the planet’s solid structure. Silicate minerals are often very complex solid crystalline structures with anions such as $\text{SiO}_4^{4-}$ and $\text{Si}_2\text{O}_8^{4-}$. Crystalline quartz is the ordered structure of silicon and oxygen ($\text{SiO}_2$), and one form of quartz has a cubic structure related to the face centered cubic arrangement (Figure 1 left, black circles = Si, white circles = O). There are also structurally disordered forms of SiO$_2$ known as silica glasses. Silica and silicates are common starting materials for chemical processes that produce more chemically useful silicon compounds, including $\text{SiCl}_4$ and elemental silicon (Figure 1 right, open circles = Si).

![Figure 1. Comparison of the cubic unit cells β-crystoballite SiO$_2$, an ordered form of silica (left) and pure elemental silicon (right). Each figure has an fcc arrangement of Si atoms.](image)

The molecule $\text{SiCl}_4$ is a very air sensitive and chemically reactive compound that is used as a starting material for a wide range of useful organometallic silicon chlorides. For example, the reaction of an alkyl Grignard with $\text{SiCl}_4$ produces alkyl chlorosilanes (Equation 1).

$$\text{SiCl}_4 + x \text{RMgCl} \rightarrow \text{R}_x\text{SiCl}_{4-x} + x \text{MgCl}_2 \quad \text{where } x = 1 - 4$$ (1)

One particularly useful product is the dichlorodimethylsilane ($\text{Me}_2\text{SiCl}_2$). This water-reactive liquid (mp = -16 °C, bp = 70°C) is a starting material for a wide range of thermally stable silicone oils and polymers with the general formula [$\text{R}_2\text{SiO}$]$_n$ (Equation 2).$^1$

$$n \text{Me}_2\text{SiCl}_2 + 2n \text{H}_2\text{O} \rightarrow \text{“n Me}_2\text{Si(OH)}_2” + 2n \text{HCl} \rightarrow [\text{Me}_2\text{SiO}]_n + n \text{H}_2\text{O}$$ (2)

For oils, $n$ is usually small and results in ring structures ($n = 3,4$; Figure 2). These ring structures may be opened up to linear chains and form fluids with high-temperature resistance ($n < 5000$) and the chains may be linked together (cross-linked) to form viscous polymers containing connected $\text{R}_2\text{SiO}$ units. The products from hydrolysis range from high-temperature heat transfer fluids, to flexible thermally stable rubber gaskets and seals, to foamed packaging materials.$^2$
Another use for SiCl₄ and chlorosilanes is in the production of elemental silicon, which is a semiconductor that has a HOMO-LUMO gap (a band gap) of 1.1 eV. It is the key material for all commercial computer chips. Inside of every computer chip is a small perfect crystal of silicon. Impure Si is usually produced from silicates that are reduced with magnesium or carbon. The resulting crude Si is then carefully melted and recrystallized to produce highly pure single crystal blocks over 12 inches in diameter. More recently the computer industry has explored ways to produce silicon films on an insulator like SiO₂. This would reduce the need to grow single crystals of Si and may allow for smaller and cheaper microelectronic devices. Conventionally silicon films are grown from a dilute gaseous mixture of SiCl₄ or H₂SiCl₂ and H₂. This reaction requires high temperatures (~ 1000 °C) to break the Si-Cl bonds and form elemental Si and HCl gas (Equation 3).

\[
\text{SiCl}_4 + 2 \text{H}_2 \rightarrow \text{Si(s)} + 4 \text{HCl(g)} \quad \Delta H_{\text{rxn}} = +294 \text{ kJ/mol} \quad \Delta S_{\text{rxn}} = 0.20 \text{ kJ/K-mol} \tag{3}
\]

Using \(\Delta G = \Delta H - T \Delta S\), a \(T = 1470 \text{ K} \quad (~1200 \text{ °C})\) is required before this reaction is spontaneous \((\Delta G < 0)\). In practice, some reaction occurs below this temperature. Under similar conditions, dichloromethylsilane could (on paper) be utilized for Si film formation (Equation 4).

\[
\text{Me}_2\text{SiCl}_2 + 2 \text{H}_2 \rightarrow \text{Si(s)} + 2 \text{HCl(g)} + 2 \text{CH}_4(g) \quad \Delta H_{\text{rxn}} = +127 \text{ kJ/mol} \quad \Delta S_{\text{rxn}} = 0.19 \text{ kJ/K-mol} \tag{4}
\]

This chemical process is much less endothermic than Equation 3 and leads to a predicted spontaneous reaction above 670 K (395 °C). One caveat to this is that a CH₄ byproduct is a good source of carbon and has been utilized extensively in diamond film synthesis. There are reports of Me₂SiCl₂ being used in an inert atmosphere near 1000 °C to produce SiC films (Equation 5).³ Silicon carbide is a commercially useful hard ceramic material related to diamond.

\[
\text{Me}_2\text{SiCl}_2 \rightarrow \text{SiC(s)} + 2 \text{HCl(g)} + \text{CH}_4(g) \quad \Delta H_{\text{rxn}} = -130 \text{ kJ/mol} \quad \Delta S_{\text{rxn}} = 0.24 \text{ kJ/K-mol} \tag{5}
\]

Since the reaction in Equation 5 is exothermic it may take place readily at moderate temperatures, before the reaction shown in Equation 4 occurs to any appreciable extent, with or without the addition of H₂. In recent years inorganic polymers have been utilized as precursors to ceramic materials; for example, polycarbosilane, \((\text{CH}_3)_2\text{Si}_n\), and related polymers have been decomposed to SiC ceramics at high temperatures.⁴

In the laboratory experiments below, we will first produce silicone oils with low values of \(n\) (Figure 2).

Figure 2. Schematic of Me₂SiCl₂ hydrolysis leading to cyclic structures [Me₂SiO]ₙ where \(n = 3, 4\).
We will use catalyzed high-temperature thermolysis (heating) to open up the oil’s ring structures and form linear polymers that are rubbery to plastic materials depending on thermolysis conditions and additives. We will perform the third part of this experiment in pairs. Each will thermally decompose some of their polymer under oxygen or inert (nitrogen) conditions.

**Experimental Timeline**

**Day 1**: Complete the Me₂SiCl₂ hydrolysis and neutralization/extraction workup step of Part 1. If there is time, remove the ether from the silicone oil.

**Day 2**: Convert the silicone oil to a cross-linked polymer. Characterize product from Part 1 product.

**Day 3**: In pairs, combine some of your polymer and place it in a ceramic boat for high temperature processing. Continue characterization of Part 1 and 2 products.

**Day 4**: Finish any product characterization and clean up your glassware.

**Experimental Procedures**

**Part 1. Synthesis of silicones via Me₂SiCl₂ hydrolysis**

*Note:* Me₂SiCl₂ is very moisture reactive and may evolve HCl vapor when exposed to air. It should be handled quickly in the hood and kept under inert conditions until the hydrolysis reaction is started.

*[In the hood]* Transfer 35 ml of Me₂SiCl₂ into a 250 ml (or 500 ml) Erlenmeyer flask containing 70 ml of degassed diethyl ether and a stirbar (cap it with a septum). Place 70 ml of H₂O in an addition funnel and Insert it into the neck of the flask. *Slowly* start dripping the water into the stirred ether solution (warning: the hydrolysis of Me₂SiCl₂ is a vigorous reaction and evolves HCl gas!). If the ether rapidly refluxes, slow the drip rate. As the reaction nears completion, you can increase the water addition rate.

*[Next steps may be done on benchtop]* After all water has been added, transfer the solution to a separatory funnel and remove the water layer. Wash the ether layer in the funnel with a dilute bicarbonate solution until it is no longer acidic (test aqueous layer with pH paper). Perform a final separatory wash with water. Dry the ether solution over anhydrous MgSO₄ in a beaker. Decant off or gravity filter the ether solution into a pre-weighed round bottom flask and remove the ether solvent using a rotary evaporator or Schlenk line. Determine the mass of your silicone oil. The silicone product is completely air stable.

**Part 1 product characterization:** IR (NaCl plates), ¹H NMR (CDCl₃)
Part 2. Conversion of dimethylsilicone oil to cross-linked silicone polymers

In a small beaker (50 or 100 ml), slowly add 5 wt % B₂O₃ (boron oxide) to a known amount of your silicone oil from Part 1, while constantly stirring with a spatula. [In the hood] Place the beaker on a hot plate and slowly and carefully heat it to ~150 ºC then up to 200 ºC. Keep heating at this temperature for 3 hours, then cool the polymeric solid to room temperature.

Part 2 product characterization: IR (KBr pellet or thin piece of pure polymer made with the IR press and placed between NaCl plates), density (see below), differential scanning calorimetry (DSC) [low T to room T, depending on instrument availability]

Density determination: Place a solid piece (~1-2 mm diameter ball with no air bubbles) of your silicone rubber polymer in a small vial. Add ~ 5 mls of acetonitrile (density = 0.79 g/ml). The polymer should sink to the bottom. Pipet in a few drops of water (density = 1.0 g/ml). Close vial and shake to mix solvents. Repeat this process until the polymer just starts to float. Weigh a known volume (~1 - 5 ml using a volumetric pipet) of the solution on the balance. Calculate density in g/ml (= g/cm³).

Part 3. Thermal conversion of borate crosslinked silicone polymer to silicon-based ceramics

This experiment has an unknown outcome and will be performed in groups of 4 with 2 boats in each of two furnaces. Once furnace will be left open to the air and another furnace will have a slow flow of nitrogen passing through it. This thermolysis/pyrolysis experiment will examine how different atmospheres affect the thermal decomposition of the silicone polymer.

[In the hood] Put ~ 5 g of polymer/per group of students (mold it into a rod-like shape) in a ceramic boat and position it near the center of a furnace (2 boats per furnace).

For the N₂ flow experiment: Put a septum with a glass tube in it (use one from a Schlenk line bubbler) on each end of the tube. Attach an oil bubbler to the one exit of the tube using Tygon tubing (see Figure 3). Hook up the other side of the tube to the N₂ gas line, set the gas flow rate at about 2 bubbles/sec, and purge out the system for 15 minutes.

For both furnaces: Set the temperature ramp rate to 5 ºC/min and start the furnace ramping to 950 ºC. Maintain this temperature for 24 hrs (TAs will shut them off).

Part 3 product characterization: IR (KBr), density (g/cm³: press pellet with hydraulic press, calculate its volume, and weigh it), X-ray diffraction.
Figure 3. Schematic of a basic inert gas flow pyrolysis system.

References


